



Aerogel as a sublimation suppression layer for thermoelectric power generation system

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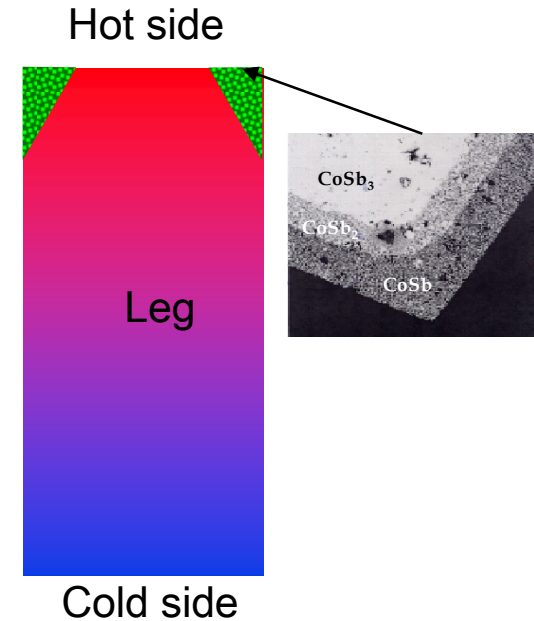
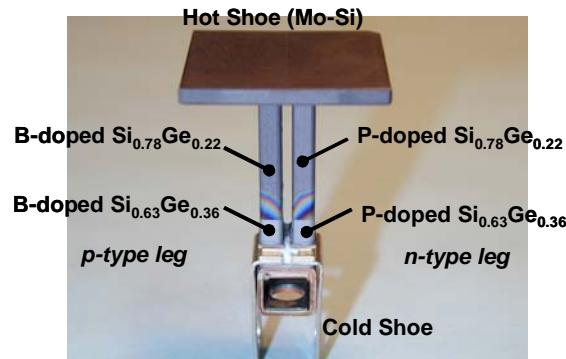
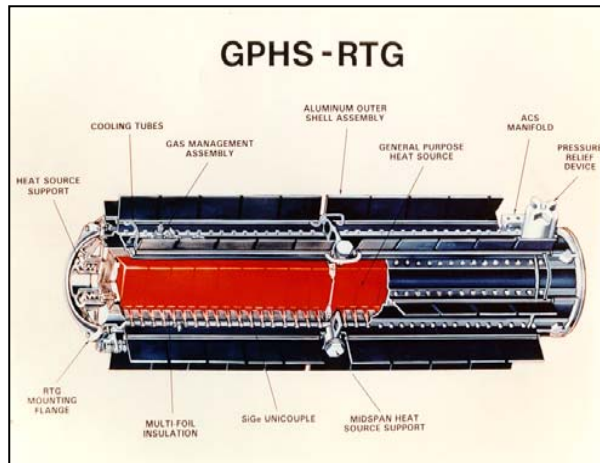
JPL/Caltech



- **Introduction**
 - Sublimation of thermoelectric materials
 - Aerogel
- **Preliminary sublimation rate measurement with aerogel**
- **Optimization of aerogel**
 - Thermal stability of aerogel
 - Shrinkage control (composite aerogel)
- **Life time sublimation rate with optimized aerogel and In-gradient test**
- **Summary and Future work**

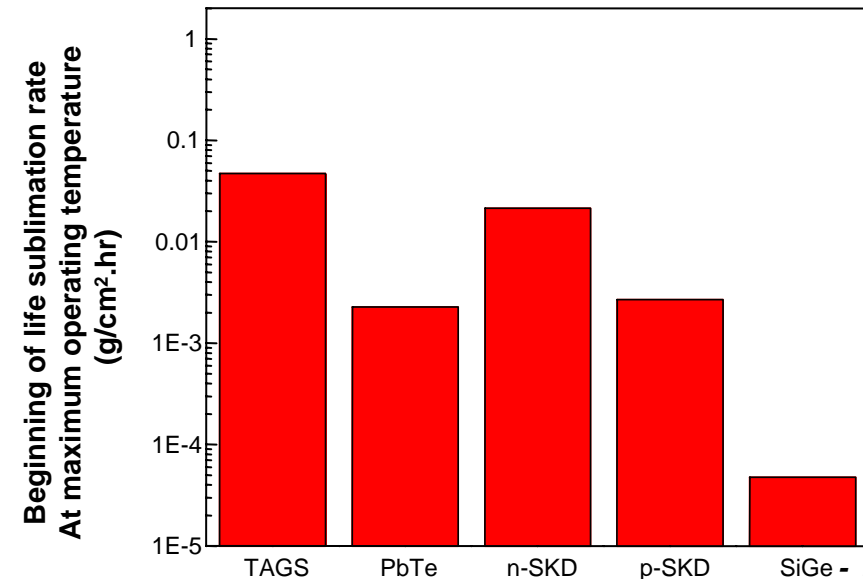


Brief background : Sublimation phenomenon and beginning of life sublimation rates



Goals:

- 1) Suppress sublimation of antimony vapor to prevent the depletion band from decomposing 5% of the effective cross section after 10 years of operation.
- 2) Contain metal vapor to prevent condensation, which can cause short circuiting on the cold side of the device
- 3) The method of suppression sublimation should not have a significant impact on the system performance



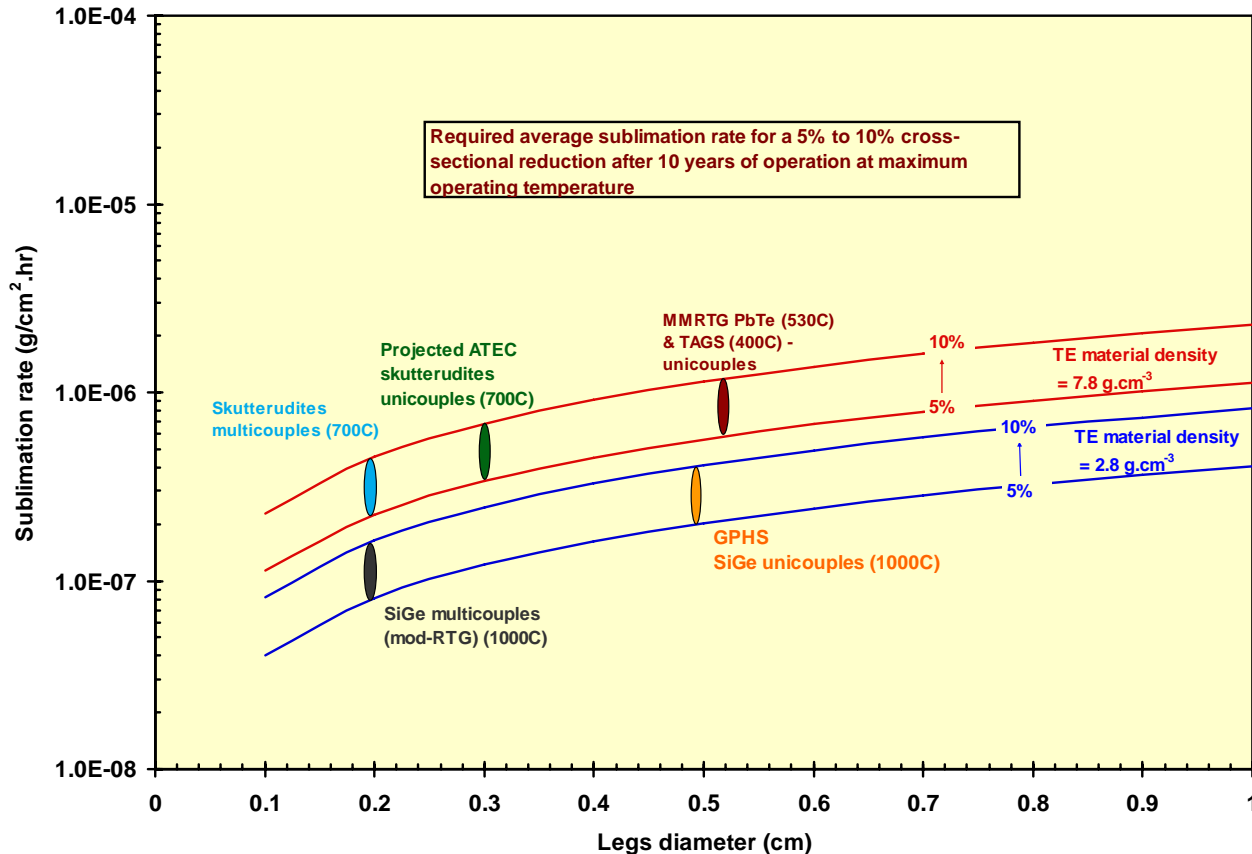


Sublimation suppression



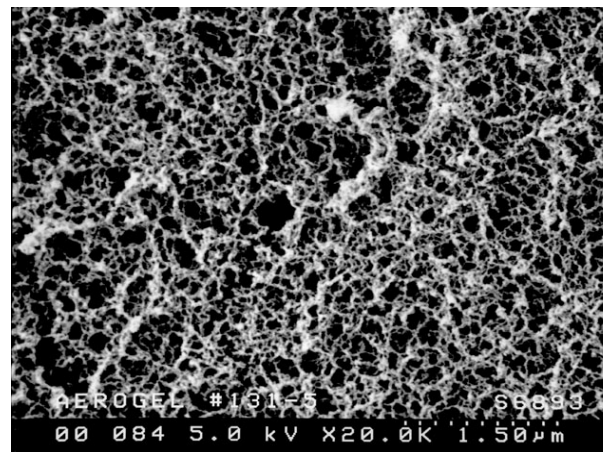
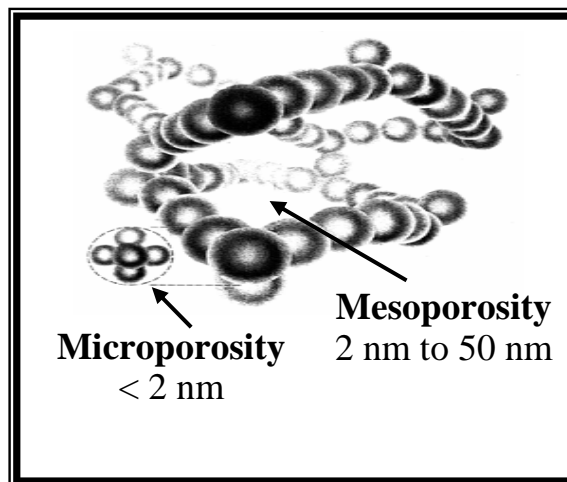
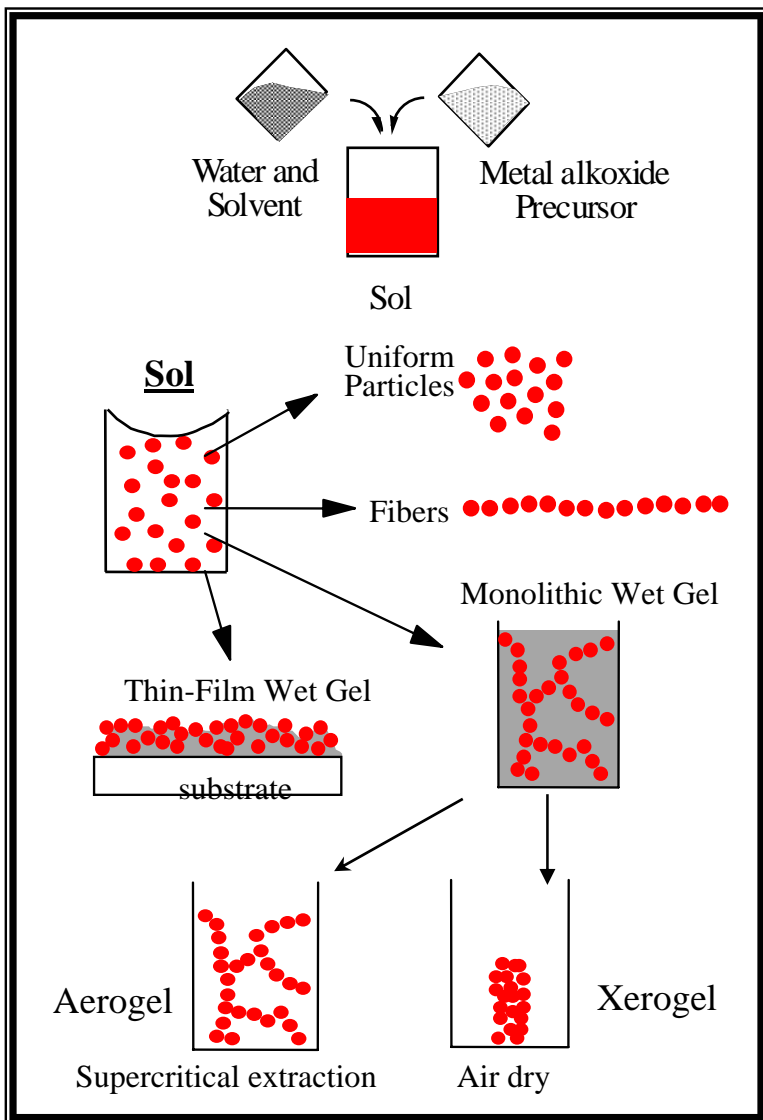
Overall objectives

- Develop sublimation suppression coating techniques
- Characterize long term efficacy of sublimation suppression coatings



Background on previous sublimation suppression methods

- SiGe RTG technology employed $\text{Si}_3\text{N}_4/\text{SiO}_2$ thin films
- PbTe/TAGS technology employed an inert cover gas



Aerogels:

- Nanometer sized particles surrounded by a continuous microporous and mesoporous volume (porosity >90%, surface area to 1000 m²/g)
- Excellent thermal and acoustic insulator (~ 15 mW/m·K at room temperature in air)



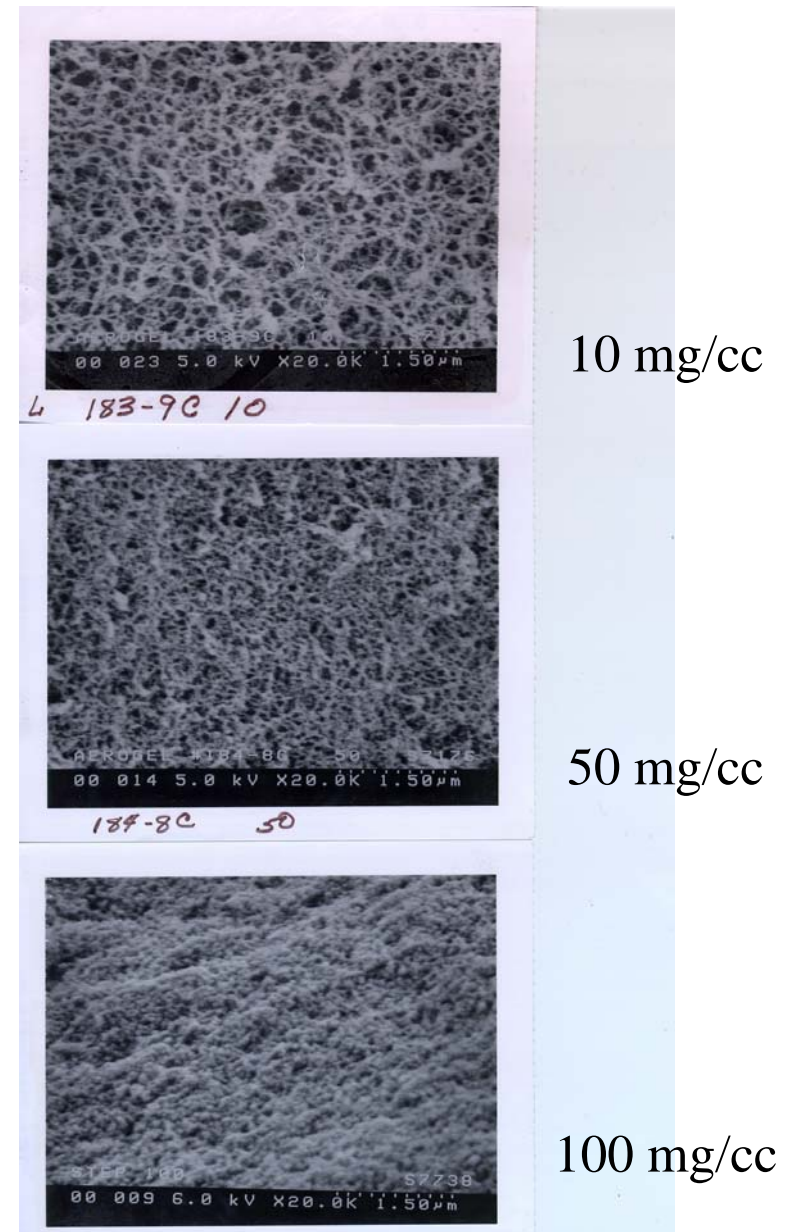
Lawrence Berkeley Lab

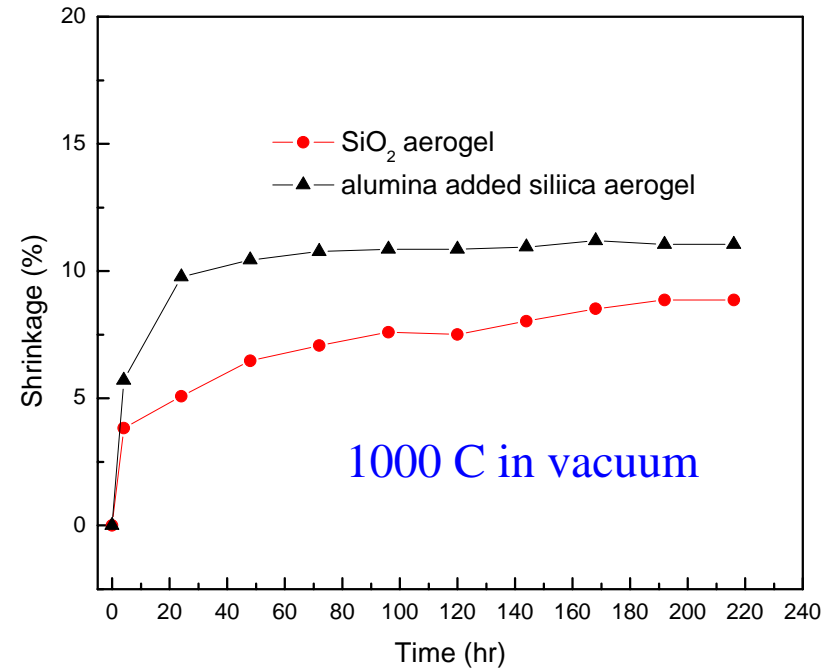
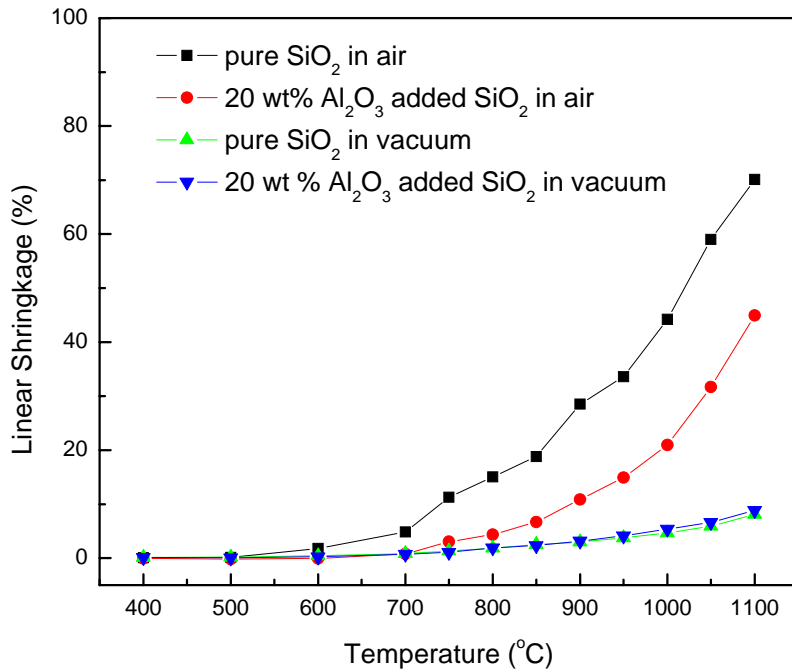
Flux through porous media

$$J = \frac{2}{3} d \frac{\varepsilon}{\tau} \sqrt{\frac{8RT}{\pi M}} \frac{dC}{dx}$$

J=Flux, d=pore diameter of porous media, ε = porosity,
 τ =tortuosity, $R=8.314 \text{ J/mol}\cdot\text{K}$, T =temperature,
 M =Molecular weight, C =concentration, x =distance

- If $d = 50 \text{ nm}$, density of aerogel = 200 mg/cc , and $x = 5 \text{ mm}$, estimated sublimation rate of Sb through aerogel at 700C is $\sim 5.85 \times 10^{-7} \text{ g/cm}^2\text{hr}$.
- Aerogel is expected to show better sublimation suppression property with increasing density.
 - Average pore diameter decreases with increasing density

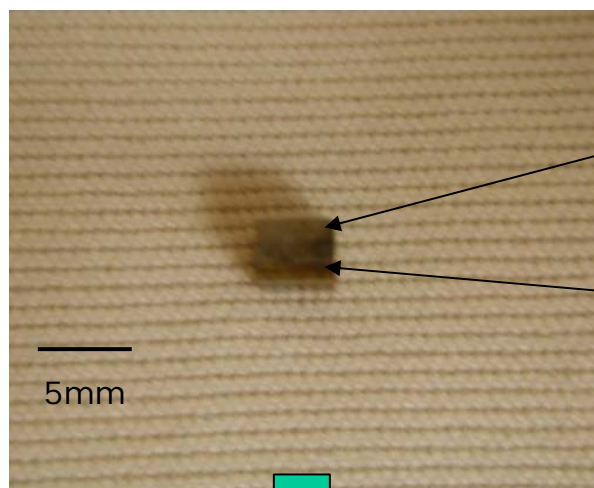




- Aerogel shows little shrinkage (~ 1%) with 700 C under vacuum.
- Most of shrinkage happens at early stage of heating, which explains long-term stability of aerogel.
- There was no detectable degradation of aerogel during coupon life test up to 6 months.

Preliminary sublimation rate measurement with TGA

Measuring Sublimation Suppression of Aerogel Coatings using the TGA



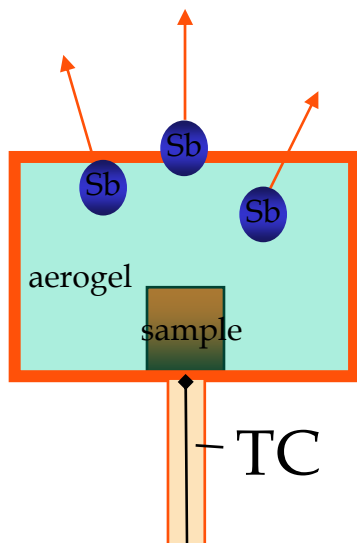
n-type SKD

Ti

5mm



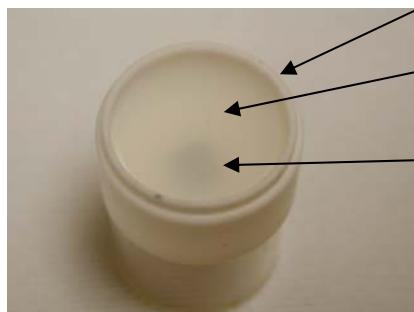
Aerogel encapsulation



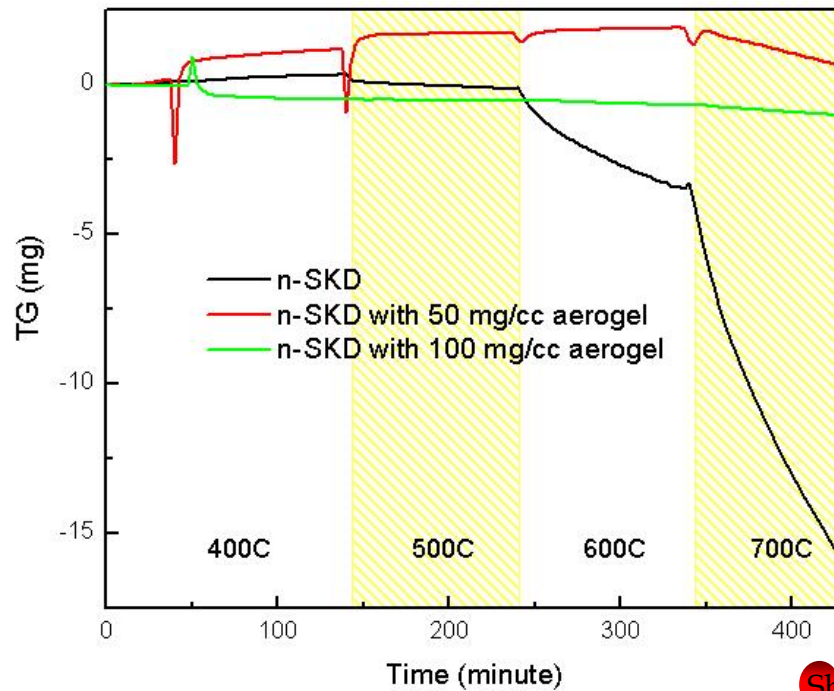
Alumina crucible

Alumina doped silica aerogel

n-type SKD covered with aerogel



Coupons tested at 700C in high vacuum (TGA)



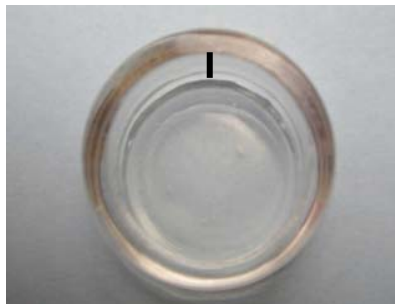
□ @ 700C

□ Uncoated: 2×10^{-2} g/cm²h

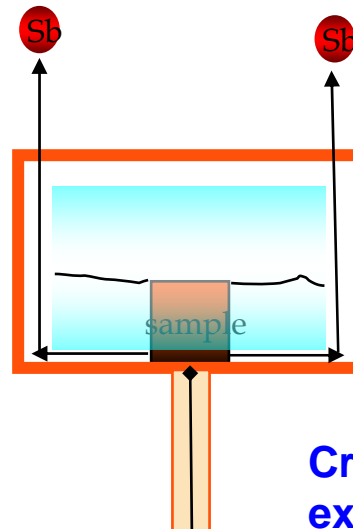
□ 50mg/cc aerogel: 3×10^{-3} g/cm²h

□ 100mg/cc aerogel: 1×10^{-3} g/cm²h

■ Demonstrated that aerogel does slow sublimation, but not as much as expected.

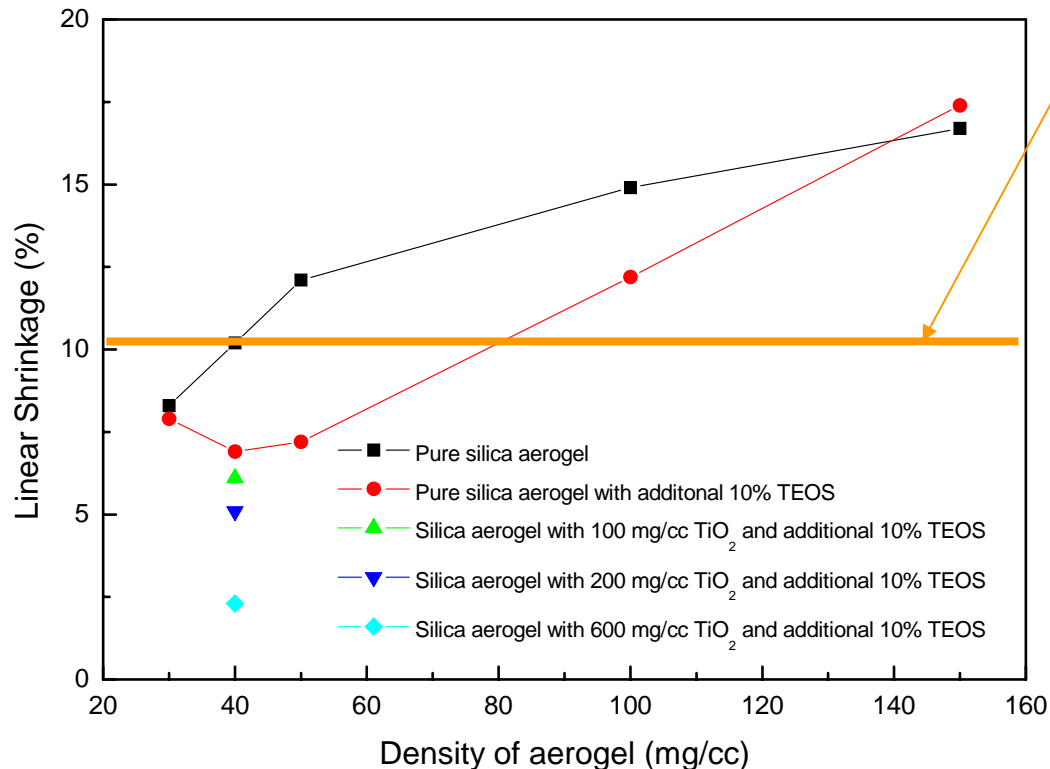


Initial sol gel process results in ~10% isotropic shrinkage



Cracks likely caused higher than expected sublimation rates

Shrinkage control of aerogel (composite aerogels)



Acceptable shrinkage level

Shrinkage reduction

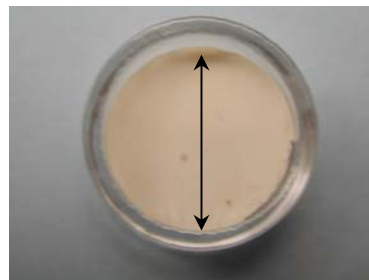
- Adding additional precursor during synthesis
- Adding solid particles to strengthen aerogel
- Changing precursor from TEOS (tetraethoxysilane) to TMOS (tetramethoxysilane)

Higher density is desirable for sublimation suppression

- Shrinkage control is required to cast crack free higher density aerogel
- Incorporating powder is another mean to increase the density of aerogel without increasing shrinkage



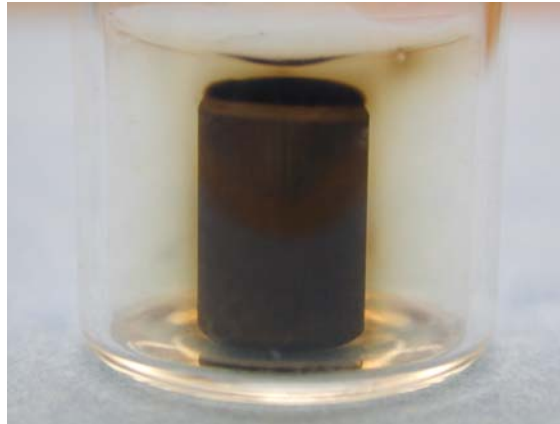
Clear aerogel



Composite aerogel

50 mg/cc

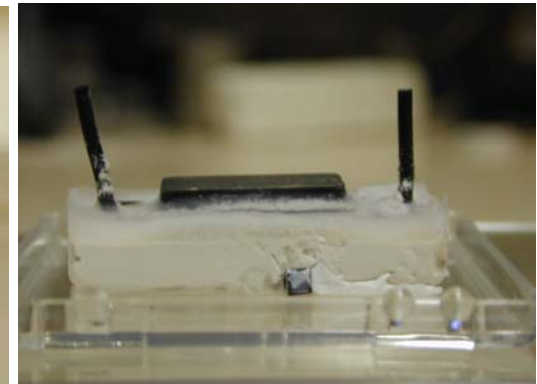
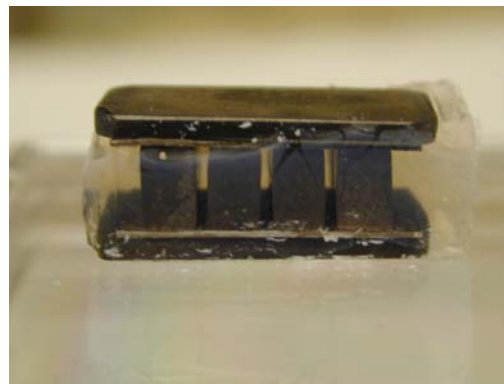
120 mg/cc



Coupons for TGA sublimation test (encapsulating a graphite cup containing an antimony puck)



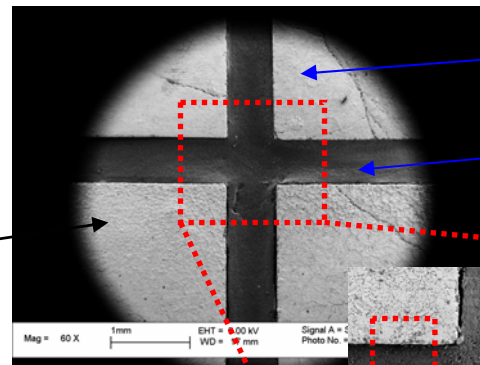
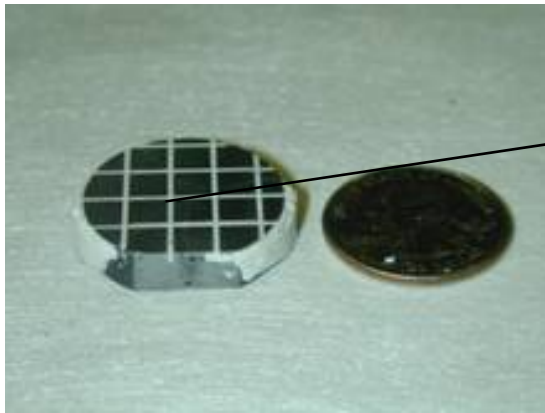
Demonstration of casting aerogel around dummy graphite legs



Encapsulation of TE modules

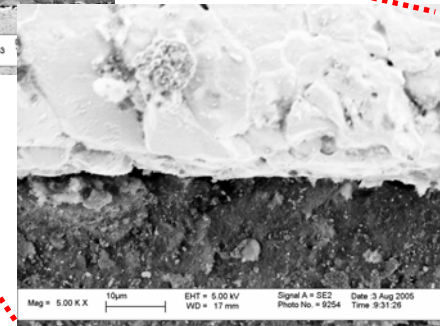
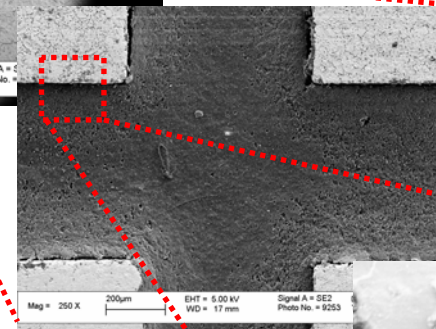
Crack free aerogel encapsulation (SEM pictures)

Current best aerogel : ~ 150 mg/cc (75 mg/cc aerogel, 20 mg/cc fumed silica, 50 mg/cc granular silica)



Skutterudite

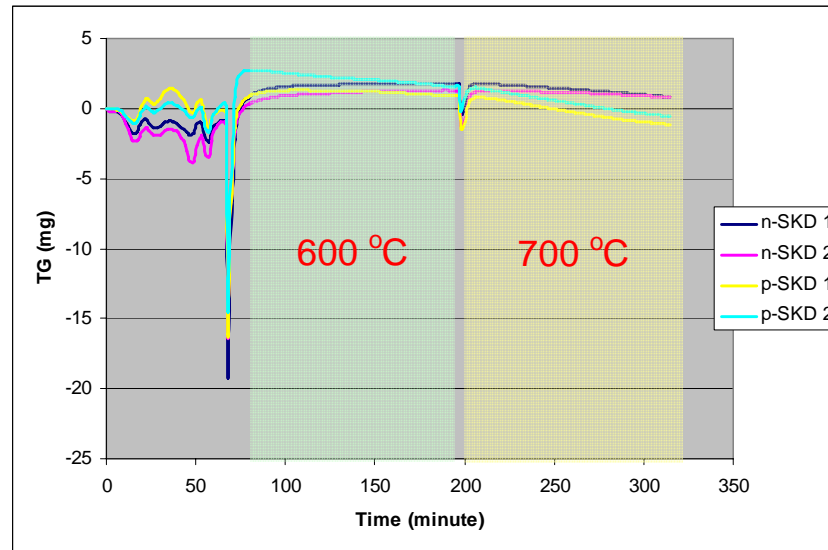
Aerogel (~150 mg/cc)



After 700C for 7 days

- SEM pictures show intimate contact between aerogel and skutterudite after 7 days at 700C under vacuum (Aerogel filled 500 µm gaps (depth ~ 5 mm) generated on skutterudite disc with checker board arrangement).

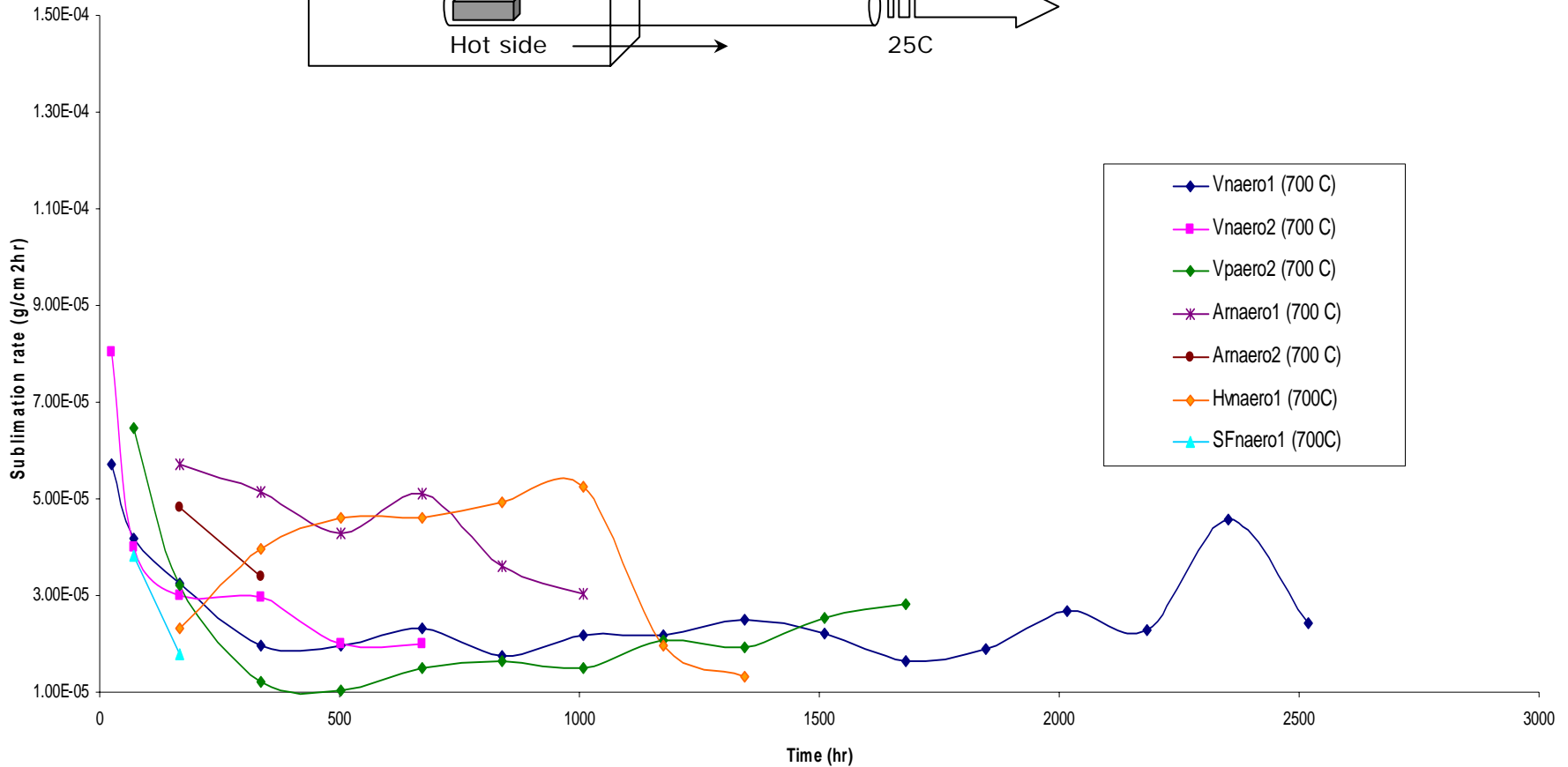
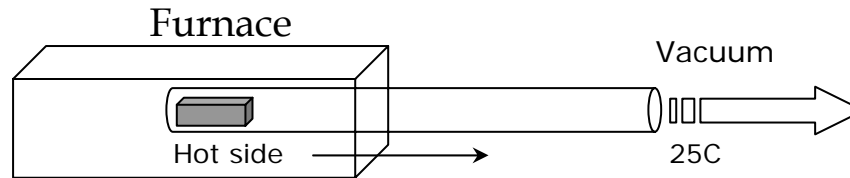
(Vacuum /Aerogel)



		Un-encapsulated (g/cm ² hr) (vacuum)	Cast aerogel (g/cm ² hr) (vacuum)
n-type skutterudite	400 °C	Not detected	Not detected
	500 °C	5.31×10^{-4}	Not detected
	600 °C	5.16×10^{-3}	Not detected
	700 °C	2.15×10^{-2}	1.15×10^{-4}

- No detectable sublimation rate at 600 °C ($< 1 \times 10^{-5}$ g/cm²hr)
- Aerogel reduced sublimation rate significantly at 700 °C and life test was set up for accurate sublimation rate measurement

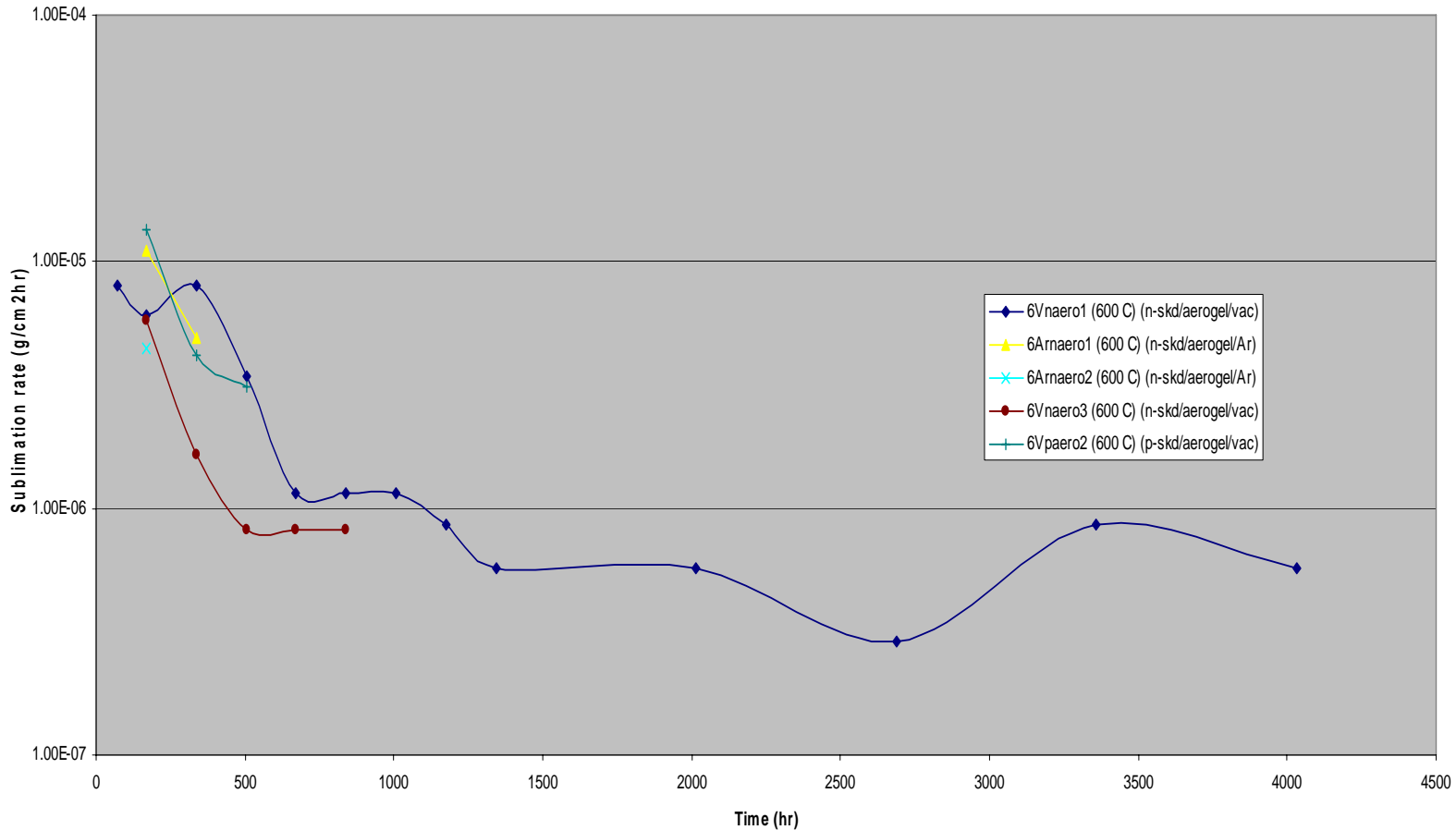
Sublimation life test (700C)



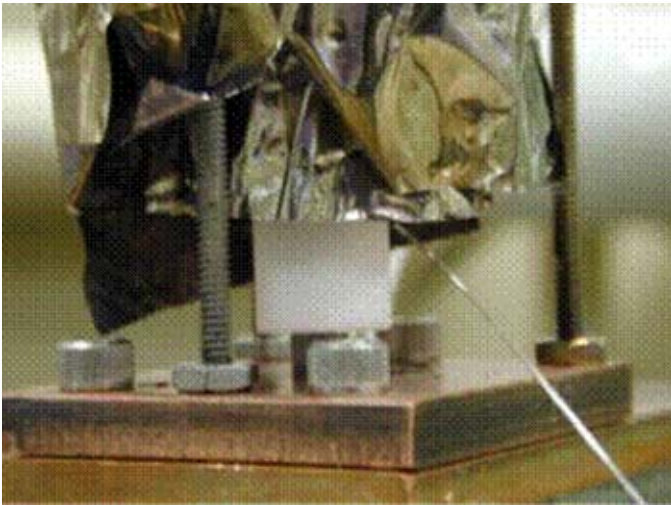
Aerogel reduces sublimation rate at 700 °C as much as 1000 times



Sublimation life test (600C)

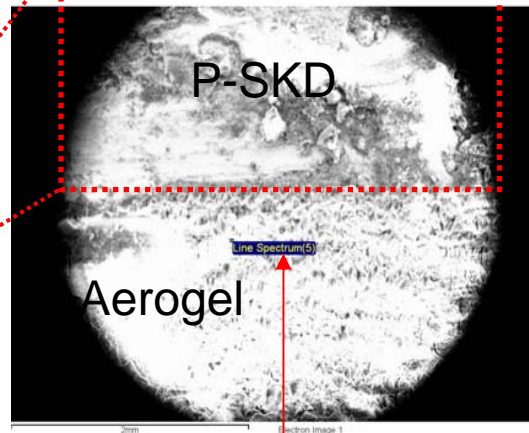
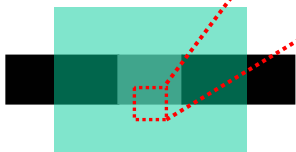


Demonstrated that desired sublimation rates ($\sim 5 \times 10^{-7}$ g/cm²hr) for 14 years of operation can be achieved up to 875K for aerogel-encapsulated low-T skutterudites after up to 4000 hours of testing

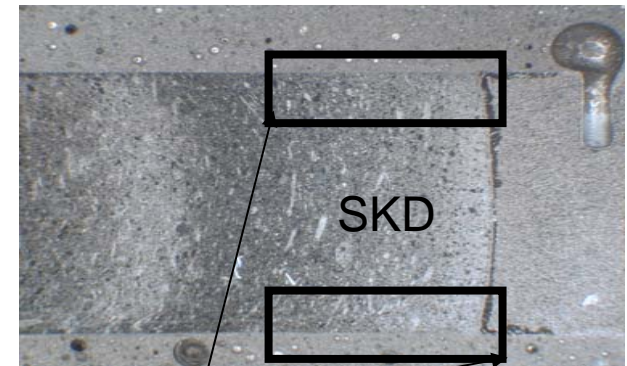


- Sb penetration into aerogel was significantly suppressed during in-gradient test due to temperature gradient across aerogel.
- Sublimation could be much slower during in-gradient test which is close simulation of real situation.

EDS after 11 days in-gradient test at 700 C

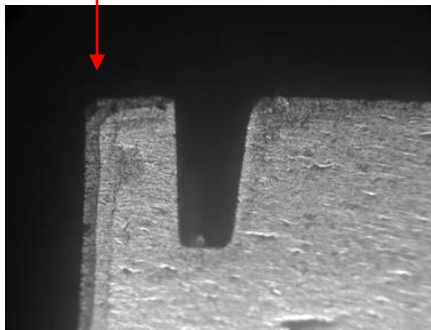
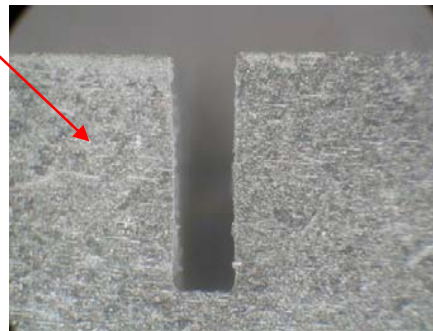
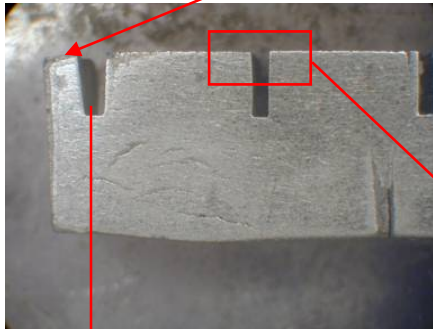
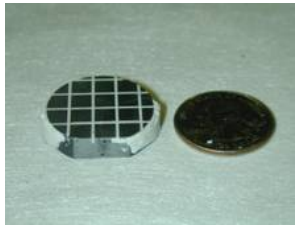


No antimony was detected



This is where depletion would be expected, but there is no apparent depletion

In gradient test (Skutterudite module after 7 days at 700C (10^{-6} torr))



- **Potential advantage of aerogel for thermoelectric power system**
 - serving as a sublimation barrier and thermal insulation simultaneously
 - easy processing by casting around structure
 - Tailoring for better thermal conductivity (adding opacifying agent)



Summary



- Aerogel process was optimized to reduce shrinkage and crack free encapsulation was demonstrated with several structures
- Aerogel reduced sublimation rate by factor of 1000 at 700 °C and $\sim 5 \times 10^{-7}$ g/cm²hr sublimation rate was achieved with aerogel coupons at 600 °C.
- Coupons were tested more than 6 months and aerogel shows no apparent degradation.
- Excellent thermal insulation properties of aerogel can improve sublimation suppression in real situation (in-gradient test).
- Additional sublimation layers are under development in order to reduce sublimation rate further at 700 °C.